

Attachment B

Description of Lawrence Berkeley National Laboratory's Catalytic Chemical Oxidation System

Introduction

Several technologies were evaluated for feasibility in the treatment of tritiated mixed wastes, considering their destruction efficiency for hazardous organic compounds, and their suitability for use with tritium. We have previously published brief reviews [1-3] of the following technologies: molten salt oxidation (MSO), supercritical water oxidation (SCWO), pulsed-corona plasma and inductively coupled plasma oxidation, catalyzed wet oxidation (DETOX^(SM)), catalytic chemical oxidation (CCO), and direct chemical oxidation (DCO).

The CCO process has been demonstrated successfully in remediation projects for organic chemical treatment and in several facilities for mixed waste treatment. The process can accommodate both organic and aqueous mixtures and achieves more than 99.999% destruction and removal efficiency (DRE). The CCO system was selected for the NTLF treatability study as the best overall match to our needs, accommodating our high tritium/low volume wastes, while confining the product tritiated water. In our study, the effective conversion of tritiated mixed waste into nonhazardous tritiated waste (tritiated water) was demonstrated using the CCO technique.

Catalytic chemical oxidation involves high-temperature decomposition of organic chemicals in the presence of a catalyst. In general, the CCO system has the following components: sample pumps, a preheater (solvent vaporizer), an oxygen source, an oxidation cell, a catalytic packed-bed reactor, liquid product collection units, and multiple tritium-emission-reduction devices. Samples are pumped into the CCO system with suitable flow rates. The temperature of the oxidation cell comes solely from the heat of combustion, while heat is provided to the catalytic reactor using a heating jacket. The oxidized and condensed liquid products (water or tritiated water) are collected in a series of condensers and a dry-ice cold trap.

CCO System Design

Two oxidation systems (see Figures 2 and 3 in the Delisting Petition) were built for comparative studies of treatment on tritiated and simulated nonradioactive surrogate samples. The knowledge gained from building the simulated nonradioactive surrogate sample oxidizer (CCO-1) was used in fabricating the tritiated-waste oxidation system (CCO-2). Both oxidizers were carefully designed to meet very high safety standards. 316 stainless steel tubing, 316 CajonTM joints, or pipe-threaded joints were used to ensure maximum structural integrity. The oxidation cell for the tritiated waste oxidizer was made of InconelTM, whereas stainless steel was used for the nontritiated waste oxidation cell.

The tritiated waste oxidizer has a control system with 11 OmegaTM CN 76000 temperature controllers equipped with auto-tune features, dual set point capability, alarms, and analog outputs. The circuit diagram was designed by NTLF staff, but the controller was built at the LBNL Electrical Fabrication Shop. The system controls the pumps, which inject the waste sample into the oxidizer. It prevents premature (underheated system) injection of samples and is also capable of shutting down the pumps and spark power supply if the oxidation cell is overheated (>550°C).

The system has a 95-db audio alarm, which will be activated if any single part of the system is overheated. For safety purposes, all alarms have been designed to be reset manually. The

power supply for the spark plugs was also built by the LBNL Instrument Repair Shop (Electronic Equipment). It supplies 30-Hz sparking at both plugs simultaneously.

Oxygen is metered into the system at the rate of 4 liters/min through the Omega™ FMA 14P2 mass flow controller to obtain a precise flow rate. The Omega™ rate meter (DPF64) also monitors the oxygen flow. If the oxygen flow rate is lower than 4.0 liters/min, the rate meter will sound an audio alarm and shut down the mixed-waste sample-feeding pump. A one-way check valve is installed at the inlet to prevent backflash into the delivery line. The efficiency of the oxidation is monitored continuously by measuring carbon monoxide and residual hydrocarbon in the exhaust gas. The temperature controllers, mass flow controller, and CO and hydrocarbon monitors are all equipped with analog output. This will allow future coupling with a personal computer for viewing and recording the process parameters.

CCO Operation Procedure

- 1) The CCO system is preheated to the following temperatures:
300°C for sample preheater
300°C for oxygen heater
500°C for the catalytic reactor filled with platinum-coated alumina pellets
150°C for all transfer lines
- 2) Samples are pumped into the system with flow rates ranging from 1.0 to 2.0 mL/min.
- 3) The temperatures of the oxidation cell are maintained in the range 450 to 550 °C.
- 4) The liquid products (HTO) are condensed and collected in a series of condensers and a dry-ice cold trap.
- 5) The liquid products are analyzed by a HP 6890 GC coupled with both flame-ionization detector (FID) and HP5973 mass-selective detector for the volatile organic compounds.
- 6) The exhaust gas from the oxidation cell and catalytic bed flows through multiple tritium-emission-reduction devices (a series of condensers, a cold trap, three water bubblers, and a silica gel filter).
- 7) The efficiency of solvent oxidation and decomposition was also monitored continuously by measuring carbon monoxide and residual hydrocarbon in the exhaust gas.

CCO Operation Inspection

LBNL staff always visually inspect, on a routine basis, the CCO system and associated equipment for leaks, spills, fugitive emissions, and signs of tampering before and after any oxidations. Prior to oxidation of any tritiated mixed waste samples or nonradioactive surrogate samples, LBNL staff also conduct an oxidation study of pure isopropanol and check the performance of the CCO system (CCO-2 or CCO-1, respectively). The oxidized liquid product generated from the oxidation of isopropanol is also analyzed using the in-house GC/MS as a part of QC procedures. (See the Treatability Study Procedure in Item 3a-d of Section 5 of the Delisting Petition for details.) The analytical results and DRE (> 99.999%) of isopropanol are always evaluated. When necessary, adjustments or modifications to the system will be made prior to oxidation of any waste samples.

Oxidation Efficiency of Organic Chemicals

From our mixed waste treatability study to date (described in the Delisting Petition), we have the following observations:

- (1) The chemical constituents listed below have been identified by GC/MS in 52 mixed waste samples oxidized in the treatability study:

acetic acid, acetic anhydride, acetone, acetonitrile, benzene, bromonitromethane, chloroform, cyclohexylamine, dimethylformamide, dioxane, ethanol, ethyl acetate, hexane, isopropanol, methylene chloride, methanol, methyl acetate, pyridine, tetrahydrofuran, tetramethylethylenediamine, toluene, triethylamine, and water.

The compositions of these mixed waste samples were all different because different tritium labeling experiments use different solvents. Each sample consists of multiple organic chemicals listed above. Some chemical constituents, such as methyl acetate, cyclohexylamine, and bromonitromethane, are the byproducts of the experiments.

- (2) Because the oxidation temperatures were always high (in the range of 450 to 550 °C) and the mixed waste samples were also oxidized in the presence of steam (steam reforming effect), the CCO system can very efficiently oxidize the volatile organic chemicals and achieve more than 99.999% of destruction and removal efficiency (DRE).
- (3) Oxidations of simulated nonradioactive surrogates using a broad range of organic chemical constituents also achieved more than 99.999% of DRE.
- (4) We believe that the high oxidation efficiency is because of (a) the high oxygen flow rate (4 liters/min) for each oxidation, and (b) the presence of steam in each sample enhances the conversion of CO to CO₂ (the water-gas shift reaction).
- (5) The liquid product (tritium-containing water) is confined and collected using multiple condensers and dry-ice cold traps in series. The exhaust gas flows through three water bubblers. The water in the three bubblers traps 1–2% of total radioactivity of the sample. Using three bubblers in a row ensures that less than 0.01% of the sample radioactivity passes through the bubbler water for absorption on the silica gel. The greater than 98% trapping efficiency for tritiated water in condensers and the cold trap of CCO-2 system greatly increase the possibility of tritium recycling.

REFERENCES

1. L.Y. Chang, C. Than, H. Morimoto, and P.G. Williams, "Treatment of Tritiated Mixed Waste by Catalytic Oxidation," presented at the ASME 4th Biennial Mixed Waste Symposium, Baltimore, MD, August 1997; published in Technology: J. Franklin Institute, 334A, 205–213 (1997).
2. L.Y. Chang, C. Than, H. Morimoto, and P.G. Williams, "A Catalytic Oxidation Study and Regulatory Analysis of Tritiated Mixed Waste," presented at Waste Management 99, Tucson, AZ, March 1999; published in Waste Management 99, in press (1999).
3. W.E. Schwinkendorf, B.C. Musgrave, and R.N. Drake, "Evaluation of Alternative Nonflame Technologies for Destruction of Hazardous Organic Waste," INEL/EXT-97-00123, Idaho National Engineering Laboratory (1997).